

Methods for producing silicon nitride films by vapor-phase growth

This invention relates to methods for producing silicon nitride films and more particularly relates to methods for producing silicon nitride films by vapor-phase growth, such as chemical vapor deposition (CVD).

Silicon nitride films have excellent barrier properties and an excellent oxidation resistance and as a consequence are used in the fabrication of microelectronic devices, for example, as an etch-stop layer, barrier layer, or gate insulation layer, and in oxide/nitride stacks.

Plasma-enhanced CVD (PECVD) and low-pressure CVD (LPCVD) are the methods primarily used at the present time to form silicon nitride films.

PECVD is typically carried out by introducing a silicon source (typically silane) and a nitrogen source (typically ammonia, but more recently nitrogen) between a pair of parallel plate electrodes and applying high-frequency energy across the electrodes at low temperatures (about 300°C) and low pressures (0.001 torr to 5 torr) in order to induce the generation of a plasma from the silicon source and nitrogen source. The active silicon species and active nitrogen species in the resulting plasma react with each other to produce a silicon nitride film. The silicon nitride films formed in this manner by PECVD typically do not have a stoichiometric composition and are also hydrogen rich and accordingly exhibit a low film density, a poor step coverage, a fast etching rate, and a poor thermal stability.

LPCVD uses low pressures (0.1 to 2 torr) and high temperatures (800°C to 900°C) and produces silicon nitride films with a quality superior to that of the silicon nitride films produced by PECVD. At the present time silicon nitride is typically produced by LPCVD by the reaction of dichlorosilane and gaseous ammonia. However, ammonium chloride is produced as a by-product in the reaction of dichlorosilane and gaseous ammonia in this LPCVD procedure: this ammonium chloride accumulates in and clogs the reactor exhaust lines and also deposits on the wafer. Moreover, existing LPCVD technology suffers from a slow rate of silicon nitride film growth and has a high thermal budget. In order to reduce this thermal budget for the production of silicon nitride films, a method has very recently been developed that produces silicon nitride films by reacting ammonia with

hexachlorodisilane used as a silicon nitride precursor. This method, however, suffers from a pronounced exacerbation of the problems cited above due to the large amounts of chlorine present in hexachlorodisilane. Silicon-containing particles are also produced by this method, which results in a substantial reduction in the life of the exhaust lines. Finally, this method can provide high-quality silicon nitride films (good step coverage ratio, low chlorine content) at excellent growth rates at a reaction temperature of, for example, 600°C, but these characteristics suffer from a pronounced deterioration when a reaction temperature $\leq 550^\circ\text{C}$ is used.

The use of carbon-containing volatile silazanes, azidosilazanes, and aminosilanes as silicon nitride precursors has been proposed in order to solve the problems cited above (refer, for example, to non-patent references 1 and 2). However, these silicon nitride precursors, whether used by themselves or in combination with ammonia, result in the incorporation of SiC and/or large amounts of carbon in the silicon nitride film product.

(Non-patent reference 1)

Grow et al., Mater. Lett. 23, 187, 1995

(Non-patent reference 2)

Levy et al., J. Mater. Res., 11, 1483, 1996

Problems to Be Solved by the Invention

The problem addressed by this invention, therefore, is to provide a vapor-phase growth method for producing silicon nitride films that can produce silicon nitride films with improved film characteristics and that can do so even at relatively low temperatures, without the accompanying generation of ammonium chloride, and without significant admixture of carbonaceous contaminants into the film product.

Means Solving the Problems

According to a first aspect of this invention, there is provided a method for producing silicon nitride films by vapor-phase growth, said method being characterized by

feeding a hydrazine gas and at least 1 precursor gas selected from the group consisting of trisilylamine gas and a silylhydrazine gas into a reaction chamber that holds at least 1 substrate and forming a silicon nitride film on said at least 1 substrate by the reaction of the two gases.

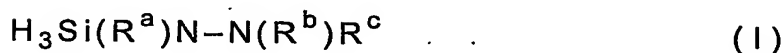
According to a second aspect of this invention, there is provided a method for producing silicon nitride films by vapor-phase growth, said method being characterized by

feeding a silylhydrazine gas into a reaction chamber that holds at least 1 substrate and forming a silicon nitride film on said at least 1 substrate by the decomposition of said silylhydrazine gas.

This invention is explained more specifically hereinbelow.

This invention, which relates to methods for forming silicon nitride films on substrates by a vapor-phase growth procedure such as CVD, employs trisilylamine ((H₃Si)₃N) and/or a silylhydrazine as silicon nitride precursors. These precursors produce a silicon nitride film by a vapor-phase reaction with a hydrazine. Among these precursors, the silylhydrazine can form a silicon nitride film by itself by thermal decomposition.

The silylhydrazine used by this invention encompasses silylhydrazine as defined by formula (I)



wherein R^a, R^b, and R^c are each independently selected from silyl, the hydrogen atom, methyl, ethyl, and phenyl.

The hydrazine that is reacted with the aforementioned precursors encompasses hydrazines defined by formula (II)



wherein R^1 , R^2 , and R^3 are each independently selected from the hydrogen atom, methyl, ethyl, and phenyl.

5 The method for producing silicon nitride film by reacting a hydrazine with the
aforementioned precursors (CVD procedure) will be described first. In this case, a
precursor gas, a hydrazine gas, and optionally an inert dilution gas are fed into a
reaction chamber that holds at least one substrate (particularly a semiconductor
substrate such as a silicon substrate) and a silicon nitride film is formed on the
10 substrate(s) by reaction between the precursor gas and hydrazine gas.

The interior of the reaction chamber can be maintained at a pressure from 0.1
torr to 1,000 torr during the reaction between the precursor gas and hydrazine gas,
while maintenance of a pressure of 0.1 torr to 10 torr within the reaction chamber is
preferred.

15

The reaction between the precursor gas and hydrazine gas can generally be
carried out at temperatures (CVD reaction temperature) no greater than 1,000°C.
However, almost no production of silicon nitride occurs at temperatures below 300°C.
Accordingly, the reaction between precursor gas and hydrazine gas can generally be
20 carried out at 300°C to 1,000°C. This precursor and the hydrazine can produce
silicon nitride at sufficiently high growth rates (film formation rate) even at low
temperatures of 400°C to 700°C. In addition, when the CVD reaction temperature is
300°C to 500°C, step coverage ratios, for example, of at least about 0.8 can be
achieved even for apertures with an aspect ratio of 10. The step coverage ratio can
25 be defined as the value afforded by dividing the minimum film thickness at a step
feature by the film thickness in a flat or planar region. The CVD reaction temperature
is usually the temperature of or near the substrate on which the silicon nitride is
formed.

The hydrazine gas and precursor gas can be fed into the reaction chamber at
30 a hydrazine/precursor flow rate ratio generally of no more than 100. While silicon
nitride can be produced even when the hydrazine/precursor flow rate ratio exceeds

100, hydrazine/precursor flow rate ratios in excess of 100 are generally uneconomical. Preferred values of the hydrazine/precursor flow rate ratio are from 1 to 80.

5 The inert dilution gas introduced on an optional basis into the reaction chamber can be an inert gas, for example, nitrogen or a rare gas such as argon.

Since neither the precursor nor the hydrazine used by this invention contains chlorine, their reaction does not generate the ammonium chloride by-product that has heretofore been a problem. Moreover, while the silylhydrazine and/or hydrazine used by this invention includes species that contain carbon, a relatively low carbon
10 concentration in the silicon nitride product has been confirmed even for the use of such carbon-containing species.

The production of silicon nitride films by the use of silylhydrazine by itself and its thermal decomposition will now be considered. In this case, silylhydrazine gas is introduced into the reaction chamber, along with any inert dilution gas used on an
15 optional basis, and a silicon nitride film is produced by thermal decomposition of the silylhydrazine. As in the CVD procedure considered above, the pressure in the reaction chamber can be maintained at from 0.1 torr to 1,000 torr, while the pressure in the reaction chamber is preferably maintained at from 0.1 torr to 10 torr.

20 As with the CVD procedure considered above, decomposition of the silylhydrazine gas can generally be carried out at temperatures from 300°C to 1,000°C. This silylhydrazine decomposition can produce silicon nitride at sufficiently high growth rates (film formation rate) even at low temperatures of 400°C to 700°C. In addition, high step coverage ratios can be achieved when the decomposition
25 temperature is 300°C to 500°C.

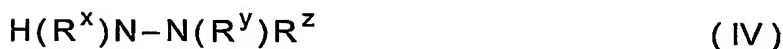
For both the CVD procedure and the thermal decomposition procedure, the silylhydrazine gas can be prepared in advance and stored in a sealed container until use or can be synthesized onsite and the gaseous reaction mixture containing the synthesized silylhydrazine gas can be introduced into the reaction chamber. A
30 silylamine gas and a hydrazine gas are introduced into a synthesis chamber in order to effect this onsite synthesis of silylhydrazine gas. At this point, an inert dilution gas, such as the inert dilution gas that may be introduced into the reaction chamber as

discussed above, can also be introduced into the synthesis chamber along with the aforementioned reaction gases. With regard to the conditions during introduction of the silylamine gas and hydrazine gas into the synthesis chamber, the pressure in the synthesis chamber should be maintained at 0.1 to 1,000 torr and the hydrazine gas/silylamine gas flow rate ratio should be 10 to 1,000. The two gases can be reacted at temperatures ranging from room temperature to 500°C. Silylhydrazine is produced by this reaction. The resulting silylhydrazine-containing gaseous reaction mixture within the synthesis chamber can then be subjected to pressure adjustment by a pressure regulator and introduced into the above-described reaction chamber.

10 The silylamine used here encompasses silylamine defined by formula (III)



wherein m is an integer from 1 to 3. The hydrazine introduced into the synthesis chamber encompasses hydrazine defined by formula (IV)



wherein R^x , R^y , and R^z are each independently selected from the hydrogen atom, methyl, ethyl, and phenyl.

Silylhydrazine (I), for example, can be produced by the reaction of the silylamine (III) and hydrazine (IV).

Figure 1 contains a block diagram of one example of a CVD-based apparatus for producing silicon nitride films that is well-suited for executing the inventive method for producing silicon nitride films. The apparatus illustrated in Example 1 uses a precursor gas source that contains already prepared precursor gas.

The production apparatus 10 illustrated in Figure 1 is provided with a reaction chamber 11, a precursor gas source 12, a hydrazine gas source 13, and a source 14 of inert dilution gas that may be introduced as circumstances dictate.

A susceptor **111** is disposed within the reaction chamber **11**, and a semiconductor substrate **112**, such as a silicon substrate, is mounted on the susceptor **111** (a single semiconductor substrate is mounted on the susceptor **111** since the apparatus illustrated in Figure 1 is a single-wafer apparatus). A heater **113** is provided within the susceptor **111** in order to heat the semiconductor substrate **112** to the prescribed CVD reaction temperature. From several semiconductor substrates to 250 semiconductor substrates may be held in the reaction chamber in the case of a batch apparatus. The heater used in a batch apparatus can have a different structure from the heater used in a single-wafer apparatus.

The precursor gas source **12** comprises a sealed container that holds liquefied precursor. The precursor gas is introduced from its source **12** through the precursor gas feed line **L1** and into the reaction chamber **11**. There are disposed in this line **L1** a shut-off valve **V1** for the precursor gas source **12** and, downstream from said shut-off valve **V1**, a flow rate controller such as, for example, a mass flow controller **MFC1**. The precursor gas is subjected to control to a prescribed flow rate by the mass flow controller **MFC1** and is introduced into the reaction chamber **11**.

The hydrazine gas source **13** comprises a sealed container that holds liquefied hydrazine. The hydrazine gas is introduced from its source **13** through the hydrazine gas feed line **L2** and into the reaction chamber **11**. There are disposed in this line **L2** a shut-off valve **V2** and, downstream therefrom, a flow rate controller such as, for example, a mass flow controller **MFC2**. The hydrazine gas is subjected to control to a prescribed flow rate by the mass flow controller **MFC2** and is introduced into the reaction chamber **11**.

The inert dilution gas source **14** comprises a sealed container that holds the inert dilution gas. As necessary or desired, the inert dilution gas is introduced from its source **14** and into the reaction chamber **11** through the inert dilution gas feed line **L3**. As shown in Figure 1, the inert dilution gas feed line **L3** can be joined with the precursor gas feed line **L1** and the inert dilution gas can thereby be introduced into the reaction chamber **11** in combination with the precursor gas. There are disposed in this line **L3** a shut-off valve **V3** and, downstream therefrom, a flow rate controller such as, for example, a mass flow controller **MFC3**. The inert gas is subjected to

control to a prescribed flow rate by the mass flow controller **MFC3** and is introduced into the reaction chamber **11**.

The outlet from the reaction chamber **11** is connected to a waste gas treatment facility **15** by the line **L4**. This waste gas treatment facility **15** removes, for example, the by-products and unreacted material, and the gas purified by the waste gas treatment facility **15** is discharged from the system. There are disposed in the line **L4** a pressure sensor **PG**, a pressure regulator such as a butterfly valve **BV1**, and a vacuum pump **PM**. The introduction of each gas into the reaction chamber **11** is carried out by the respective mass flow controllers, while the pressure within the reaction chamber **11** is monitored by the pressure sensor **PG** and is established at a prescribed pressure value by operation of the pump **PM** and control of the aperture of the butterfly valve **BV1**.

When the silicon nitride film is to be produced by thermal decomposition of the silylhydrazine gas, use of the hydrazine feed system (the source **13**, feed line **L2**, shut-off valve **V2**, and mass flow controller **MFC2**) becomes unnecessary and it need not be provided.

Figure 2 contains a block diagram that illustrates an apparatus for producing silicon nitride films that contains an onsite facility for producing silylhydrazine. Those constituent elements in Figure 2 that are the same as in Figure 1 are assigned the same reference symbol and their detailed explanation has been omitted.

The production apparatus **20** illustrated in Figure 2, in addition to having the same type of reaction chamber **11** as the one illustrated in Figure 1, contains a synthesis chamber **21** for the onsite synthesis of silylhydrazine. A heater **211** is disposed on the circumference of this synthesis chamber **21** for the purpose of heating the interior of the synthesis chamber **21** to the prescribed reaction temperature.

The production apparatus **20** illustrated in Figure 2 lacks the precursor gas source **12** shown in Figure 1 and contains a source **22** of a silylamine that will react with the hydrazine to produce a silylhydrazine. The silylamine source **22** comprises a sealed container that holds the silylamine in liquid form. Silylamine gas is introduced from this source **22** through the feed line **L21** and into the synthesis chamber **21**. There are disposed in the line **L21** a shut-off valve **V21** and, downstream therefrom,

a flow rate controller such as, for example, a mass flow controller **MFC21**. The silylamine gas is subjected to control to a prescribed flow rate by the mass flow controller **MFC21** and is introduced into the synthesis chamber **21**.

The hydrazine gas source **13** is provided with a feed line **L22** to the synthesis chamber **21** in addition to the feed line **L2** to the reaction chamber **11**. There are disposed in this feed line **L22** a shut-off valve **V22** and, downstream therefrom, a flow rate controller such as, for example, a mass flow controller **MFC22**. The hydrazine gas is subjected to control to a prescribed flow rate by the mass flow controller **MFC22** and is introduced into the synthesis chamber **21**.

The inert dilution gas source **14** is provided with a feed line **L23** to the synthesis chamber **21** in addition to the feed line **L3** to the reaction chamber **11**. There are disposed in this feed line **L23** a shut-off valve **V23** and, downstream therefrom, a flow rate controller such as, for example, a mass flow controller **MFC23**. As necessary or desired, the inert dilution gas is subjected to control to a prescribed flow rate by the mass flow controller **MFC23** and is introduced into the synthesis chamber **21**. The line **L3** in the apparatus in Figure 2 is directly connected to the reaction chamber **11**.

The outlet from the synthesis chamber **21** is connected by the line **L24** to the reaction chamber **11**. A pressure regulator, for example, a butterfly valve **BV2**, is provided in the line **L24**. The silylhydrazine gas-containing gaseous reaction mixture afforded by the synthesis chamber **21** is introduced into the reaction chamber **11** after the pressure in the synthesis chamber **21** has been adjusted by the butterfly valve **BV2** as appropriate for introduction into the reaction chamber **11**.

With regard to the handling of the precursor gas in the apparatus illustrated in Figure 1 for producing silicon nitride films, the gas-phase material is withdrawn from the precursor gas source **12** — which holds the precursor gas in liquid form — and is introduced into the reaction chamber **11** via the line **L1** by opening the valve **V1** and carrying out adjustment using the mass flow controller **MFC1**. However, the precursor gas can also be introduced into the reaction chamber **11** through the line **L1** using a bubbler or vaporizer. Figure 3 illustrates a precursor gas feed system that uses a bubbler. This feed system, which is used in place of the precursor gas source **12** and the valve **V1** in the production apparatus illustrated in Figure 1, is provided

with a precursor gas source **32** that holds precursor gas **31** in liquid form. The line **L31** is inserted into this precursor gas source **32** in order to bubble inert gas from a source **33** of the same inert gas as described above into the liquid precursor gas **31** held in the precursor gas source **32**. A shut-off valve **V31** is disposed in the line **L31**.

5 The line **L1** shown in the production apparatus of Figure 1 is inserted into the precursor gas source **32** above the liquid surface of the liquid precursor gas **31**. A shut-off valve **V32** is disposed in the line **L1**. Precursor becomes entrained in the inert gas when the inert gas is bubbled therein and is introduced into the reaction chamber **11** shown in Figure 1 through the line **L1** while being subjected to flow rate control by the mass flow controller **MFC1**.

Figure 4 illustrates a precursor gas feed system that uses a vaporizer. This feed system, which is used in place of the precursor gas source **12** and the mass flow controller **MFC1** in the production apparatus illustrated in Figure 1, is provided with a precursor gas source **42** that holds precursor gas **41** in liquid form. A line **L41** is provided to this precursor gas source **42** in order to introduce inert gas from a source **43** of the same inert gas as described above, in such a manner that the liquid surface of the liquid precursor gas **31** is pressed by the inert gas. A shut-off valve **V41** is disposed in the line **L41**. In addition, the line **L1** in the production apparatus illustrated in Figure 1 is inserted into the precursor gas source **42** into the liquid precursor gas **41** itself. There are provided in this line **L1** a shut-off valve **V42**, a liquid mass flow controller **LMFC41** downstream therefrom, and a vaporizer **44** downstream from the liquid mass flow controller **LMFC41**. The liquid precursor **41** pressed out by the introduction of inert gas from the inert gas source **43** flows through the line **L1** and is subjected to flow rate control by the liquid mass flow controller **LMFC41** and is introduced into the vaporizer **44**. The liquid precursor is vaporized in this vaporizer **44** and is then introduced into the reaction chamber **11** shown in Figure 1. Inert gas can also be introduced into the vaporizer **44** through the line **L42** from the inert gas source **45** in order to promote vaporization of the liquid precursor in the vaporizer **44**. There are disposed in this line **L42**, for example, a mass flow controller **MFC42** in order to control the flow rate of inert gas from the inert gas source **45** and, downstream from said mass flow controller **MFC42**, a shut-off valve **V43**.

Examples

This invention will be described in additional detail by working examples as follows, but this invention is not limited to these working examples.

Example 1

This example used a production apparatus with the structure illustrated in Example 1. Silicon nitride films were produced on silicon substrates at different CVD reaction temperatures (T) while introducing TSA gas at a feed flow rate of 0.5 sccm or 4 sccm and 1,1-dimethylhydrazine (UDMH) gas at a feed flow rate of 40 sccm into a reaction chamber that held a silicon substrate. The pressure within the reaction chamber was maintained at 1 torr. The silicon nitride deposition (growth) rate was measured during this process, and the obtained values are plotted logarithmically in Figure 5 against 1,000 times the reciprocal of the reaction temperature (T in K). Line a in Figure 5 plots the results for the feed of 0.5 sccm TSA gas (UDMH/TSA feed flow rate ratio = 80), while line b plots the results for a TSA gas feed of 4 sccm (UDMH/TSA feed flow rate ratio = 10).

As may be understood from the results in Figure 5, the silicon nitride film growth rate was larger at the smaller UDMH/TSA feed flow rate ratio and increased with increasing reaction temperature. However, the silicon nitride film growth rate was still high enough for practical applications even at a temperature as low as 480°C.

The composition of the obtained silicon nitride films as measured by Auger elemental analysis and ellipsometry was $\text{Si}_{0.8-0.9}\text{N}$. The carbon content of the silicon nitride films prepared at a UDMH/TSA feed flow rate ratio of 80 was only 3 weight%. The etching rate of the individual silicon nitride films by 0.25% aqueous hydrogen fluoride was measured at 30-50 Å/min in all cases, which is substantially lower than the etching rate of silicon nitride films afforded by PECVD.

The gaseous reaction mixture within the reaction chamber was also analyzed by Fourier transform infrared spectroscopy (FTIR) in this example. It was confirmed at both UDMH/TSA feed flow rate ratios that (a) the intensity ratio

($I(947)/I(2172)$) for the two main peaks for TSA (the peak at about 947 cm^{-1} assigned to the SiN bond and the peak at about 2172 cm^{-1} assigned to the SiH bond) underwent a change (see Figure 6) and (b) the peak assigned to the SiH bond shifted from 2172 cm^{-1} to 2163 cm^{-1} . These facts confirm that

5 disilyldimethylhydrazine ($(\text{SiH}_3)_2\text{N}-\text{N}(\text{CH}_3)_2$) was produced by the reaction of TSA and UDMH at temperatures $\geq 450^\circ\text{C}$ (see Figure 6). The correlation and synthesis of the facts associated with the production of silicon nitride films in this example enables the following to be said:

- (i) silylhydrazine can be used as precursor;
- 10 (ii) silylhydrazine can be produced by the reaction of a silylamine and a hydrazine; and
- (iii) silicon nitride can be produced using the silylhydrazine-containing gaseous reaction mixture produced by the reaction of a silylamine and a hydrazine.

15 Example 2

Using a production apparatus with the structure shown in Figure 1, silicon nitride films were formed at different reaction temperatures in a reaction chamber holding a silicon substrate on which trenches (diameter: $0.6\text{ }\mu\text{m}$) with an aspect ratio (depth/diameter) of 10 had been formed. UDMH was introduced at a flow rate of 40

20 sccm; TSA gas was introduced at a flow rate of 4 sccm; and a pressure of 1 torr was established in the reaction chamber. The step coverage ratios of the silicon nitride films obtained at the different temperatures were measured by scanning electron microscopy (SEM), and the results are reported in Figure 7.

The results reported in Figure 7 not only show that the step coverage ratio of

25 the silicon nitride film product can be improved to about 0.8 by establishing the reaction temperature at 500°C , but also enable the prediction that the step coverage ratio can be improved still further by setting the reaction temperature at even lower values.

This invention has been described hereinabove through various embodiments

30 and working examples, but this invention is not limited thereto. The various embodiments described above can be combined.

As has been described hereinabove, the inventive methods are not accompanied by the production of ammonium chloride, avoid significant admixture of carbonaceous contaminants in the film products, and also enable the production of silicon nitride films with better film properties even at relatively low temperatures.

5

Brief Description of the Drawings

Figure 1 contains a block diagram that illustrates an example of an apparatus for producing silicon nitride films.

10 Figure 2 contains a block diagram that illustrates another example of an Apparatus for producing silicon nitride films.

Figure 3 contains a block diagram of a precursor gas feed system that uses a bubbler.

Figure 4 contains a block diagram of a precursor gas feed system that uses a vaporizer.

15 Figure 5 contains a graph that shows the relationship between the CVD reaction temperature and the silicon nitride film growth rate.

Figure 6 contains a graph that shows the relationship between the intensity ratio between the two main peaks for TSA and the reaction temperature.

20 Figure 7 contains a graph that shows the relationship between the CVD reaction temperature and the step coverage ratio for silicon nitride films.